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SEALED PRIMARY
LITHIUM - INORGANIC ELECTROLYTE CELL

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report summarizes the R&D activities carried out by P. R. Mallory & Co. on the ECOM contract DAAB-07-74-C-0109 from 1 October 1977 to 31 December 1977. A previous interim report (ECOM-74-0109-13) issued on November 1977 summarized all the activities carried out in this contract from March 1974 to July 1977.

The objective of this program is to develop a D cell which is storable and ⟶ over

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operable in the temperature range of -40 to 160°F and is capable of delivering in excess of 150 WHr/lb at the thirty hour rate and peak power density of 50 watts/lb and a capacity degradation of less than 10% after one month of storage at 160°F. We showed that all the above objectives can be met by the hermetic $Li/SOCl_2$ D cells developed by us. In fact, the low rate D cells developed by us on a separate program delivered capacities of 18 A.Hr at a constant voltage of 3.5 volt corresponding to an energy density of 290 WHr/lb and 20 WHr/in^3 at low drains (0.01-0.03A). High rate cells routinely delivered 12 A.Hr at 1.0A drain corresponding to energy density of 156 WHr/lb and 11 WHr/in^3. ⟶ CU IN.

However, we found that the system suffered from two inherent deficiencies; a voltage delay and an explosion hazard. We solved the voltage-delay problem, but the explosion hazard problem remains unsolved to date. The most serious concern involves the fact that a completely discharged cell while sitting on the shelf at 25°C occasionally explodes without any warning. This indicates that discharge creates instability in the cells.

During the last quarter we characterized this instability by doing differential thermal analysis of discharged D cells. We found that sharp exothermic reactions occur in 80-100°C temperature range and that the chemicals responsible for these reactions are consumed during the first thermal cycle. Thus, controlled thermal excursion may be one of the ways to deactivate the discharged cells. The efficacy and the practicality of this approach is yet to be ascertained.

Some experimental support for the 'hot spot' theory of cell explosion has also been obtained.

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I. Introduction

The R&D activities carried out by P. R. Mallory & Co. on the development of a primary Li/SOCl$_2$ D cell from March 1974 to July 1977 on this contract was summarized in an interim report (1) issued in Nov. 1977. The original objective of this program was to develop a D cell which is storable and operable in the temperature range of -40 to 160°F and is capable of delivering in excess of 150 WHr/lb at the thirty hour rate and peak power density of 50 watts/lb and a capacity degradation of less than 10% after one month of storage at 160°F.

We carried out a systematic investigation of the system in an effort to define the intrinsic performance capabilities as well as the limitations of the system. Our basic approach was two fold:

(a) Optimization of the system in order to achieve all the above performance goals in a hermetically sealed D cell structure, and

(b) the identification and definition of problems associated with the system and the development of approaches to solve these problems.

We showed that all the above objectives can be met by the hermetic Li/SOCl$_2$ D cells developed by us. In fact, the low rate D cells developed by us on a separate program delivered capacities of 18 A.Hr at a constant voltage of 3.5 volt corresponding to an energy density of 290 WHr/lb and 20 WHr/in^3 at low drains (0.01-0.03A). High rate cells routinely delivered 12 A.Hr at 1.0A drain corresponding to energy density of 156 WHr/lb and 11 WHr/in^3.

However, we found that the system suffered from two inherent deficiencies:

(a) A voltage delay, particularly at low temperatures after high temperature storage.

(b) A chemical instability that led to an explosion hazard, particularly on shorting and forced as well as on resistive load overdischarge.

We studied the voltage-delay problem in sufficient detail to define its underlying causes and developed several methods for alleviating it. Lowering the electrolyte salt (LiAlCl$_4$) concentration as well as a partial discharge alleviated the voltage delay to an extent that the cells show no voltage delay after a storage of 1 month at 72°C and test at -30°C at currents of 0.25, 1.0 and 3.0A. We consider the problem to be essentially solved for

all practical purposes.

We investigated the explosion hazard problem in a phenomenological manner. First we established the conditions under which the hermetic Li/SOCl$_2$ D cells explode. Then we attempted to develop ways and means to prevent the explosion. We found that the lowering of the rate capability may not prevent cell explosions as long as the cell can get hot enough by other extraneous circumstances such as high temperature storage, heavy insulation of the cell wall and so on. We found that low pressure venting is an effective way of preventing cell explosions in external shorts. However, this approach was ineffective in preventing explosions from forced over-discharge. Also, on occasion the cells exploded on resistive load over-discharge. A completely discharged battery, while sitting on the shelf at 25°C, may also explode quite unexpectedly. This is of concern since it is impossible to prevent resistive load overdischarge and/or storage of partially and/or completely discharged batteries in normal use. We believe that this problem needs to be solved before the field use of the system can be recommended, particularly in regard to D size cells.

We carried out DTA (Differential Thermal Analysis) studies of the chemical compounds and their mixtures that may be present in a partially discharged Li/SOCl$_2$ cell and identified the exothermic reactants that might either initiate or propagate an explosive reaction in the system. However, we have not been able to develop a suitable inhibitor for quenching those exothermic reactions as yet. We also found a plausible mechanism for the observed spontaneous explosion of partially discharged cell on storage. Although we identified some safe design features for a Li/SOCl$_2$ cell we have not yet found an entirely satisfactory chemical solution to the explosion problem.

We continued our investigations to develop approaches to alleviate the problem of spontaneous thermal runaway of discharged Li/SOCl$_2$ hermetic D cells. The latest results are reported here.

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II. Differential Thermal Analysis of Hermetic Li/SOCl$_2$ D Cells

We found (1) the undischarged Li/SOCl$_2$ hermetic D cells to be more stable and predictable than the discharged cells. Also, the thermal runaways experienced by the undischarged D cells on accidental shorting (internal or external) was intrinsically preventable by means of low pressure venting. No such prevention was possible in the case of spontaneous thermal runaway of discharged cells. The latter is also unpredictable. The purpose of this study is to identify and characterize the nature of the instability that may have been generated as a result of the discharge of the Li/SOCl$_2$ D cells. We chose to use a thermal method to characterize the instability of the hermetic D cells since this is the most direct approach and the results may complement our earlier DTA results (1) of cell constituents.

A.   Experimental

Hermetic D cells were made by winding carbon cathodes (20" x 1.75" x 0.025"), Li anodes (21.25" x 2.0" x 0.015") and two layers of glass filter paper separators into cylindrical spools and packaging them in D size (OD: 1.30", L: 2.38") nickel cans. The cell top was designed with three feedthroughs, two of which are tubes extending halfway down the cell. The tubes are closed at the bottom end and are used as thermocouple wells. The third (short) feedthrough is also a tube and it acts both as an electrolyte fill port and the anode terminal. This tube is closed at the top after the electrolyte filling. The cross-sectional view of the cell is shown in Fig. 1. The thermocouple well that was used for the differential temperature measurements was the one located halfway between the center and the wall of the cell.

The cross-sectional view of the heating fixture developed for carrying out the DTA of the D cells is shown in Fig. 2. It consists of a split aluminum block with two cylindrical cavities for the D cells and three thermocouple wells located at three positions shown in Fig. 2. The two halves of the aluminum block are put together after placing the two D cells in the proper cavities and securing them by means of screws. In this manner good thermal contact is ensured between the D cell and the aluminum block. The aluminum block is then wrapped with heating elements which are connected to a power supply that provides an approximately linear temperature rise. The aluminum fixture is thoroughly insulated on all sides to prevent heat dissipation.

The DTA of D cells was carried out by heating the aluminum fixture so that the temperature of the fixture rose approximately linearly and monitoring the differential temperature of the two D cells, one of which served as the reference.

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B.   Results

The sensitivity of the DTA system was checked by running a DTA of two undischarged D cells. The thermogram is shown in Fig. 3. The differential temperature response is shown in milivolts and the temperature of the aluminum fixture is shown in °C. The temperature limit of the experiment was kept relatively low, viz. between the room temperature and 70°C. The heating rate was approximately 0.2°C/minute. The absence of any transitions indicate that the D cells were identical in terms of their thermal properties. The open circuit voltage (OCV) of both the cells was monitored during the experiment. It was 3.59V at 25°C and it decreased to 3.57V at 70°C.

A DTA run of an undischarged D cell using another D cell filled with Al_2O_3 as a reference is shown in Fig. 4. The gradual drift of the differential temperature at the start is attributed to the difference in the thermal characteristics of the $Li/SOCl_2$ cell and the reference cell. Again, the absence of any transitions indicate that Al_2O_3 filled D cells can be used as a reference cell. The temperature was increased to almost 100°C in this run.

Next, we discharged a D cell at 0.25A to remove 6 A.Hr of its capacity and then ran a DTA of this partially discharged D cell against a D size can filled with Al_2O_3. The thermogram is shown in Fig. 5. The initial drift was due to Al_2O_3 as before. A very broad exothermic peak around 80°C was observed. A second run, Fig. 6, using the same discharged cell and a fresh cell as reference, showed no exothermic transitions. The use of fresh cell as a reference instead of Al_2O_3, prevents the drifting of the base line of the thermogram.

In the above runs we kept the upper limit of the temperature at 100°C. In the next run we increased the upper limit of the temperature to 163°C. The thermograms of two fresh cells are shown in Fig. 7. The absence of the drifting base lines as well as the absence of any transitions indicate that the fresh cells are quite similar in their thermal characteristics up to 163°C. An upper temperature limit of about 170°C was maintained for all the subsequent runs.

The D cell which was discharged at 6 A.Hr and subjected to DTA runs earlier was discharged further at 0.25A for an additional capacity of 7.1 A.Hr; thus making the total removed capacity 13.1 A.Hr. This discharged cell was used again for a DTA run with a fresh cell as a reference. The thermogram showed no transitions from room temperature up to 70°C. The thermogram at temperatures between 70° and 163°C is shown in Fig. 8. The average heating rate was 0.35°/minute. The thermogram showed two exothermic peaks closed together at 92° and 103°; and a third smaller one at 148°C. A repeat run, as shown in Fig. 9, showed no transitions.

Another D cell was discharged completely at 0.25A, realizing a capacity of 12.7 A.Hr. The DTA thermogram of this cell with a fresh cell as a reference is shown in Fig. 10. There are two sharp exothermic peaks at

99° and 112° followed by the beginning of another exothermic peak at 164°. The sharpness of the peaks and the increase of the peak temperatures of this run compared to the previous run (Fig. 8) may be due to the increased heating rates, 0.8°C/minute which is more than twice that of the previous run. The exothermic behavior of the discharged cell appears to be reproducible. The repeat run of the same cells (Fig. 11) showed no transitions as before.

We discharged another D cell at 0.25A and realized a capacity of 12.0 A.Hr to 2.0 volt. This cell was also subjected to a DTA run using Al_2O_3 (in D can) as reference. The thermogram is shown in Fig. 12. The two sharp exotherms at 90° and 113° followed by the beginning of a third one at 166° are very similar to the ones seen in the previous run. The apparent endotherm at 133° is most likely due to the drifting of the base line. The reproducibility of the phenomenon appears to be quite good. The repeat run of the same cell, (Fig. 13) shows no exothermic transitions except towards the end of the thermogram, where it shows the beginning of an exothermic transition.

We measured the differential temperatures of another D cell during the course of its discharge at 0.25A using Al_2O_3 as reference. We found that the differential temperature remained virtually constant during the discharge and began an exothermic rise towards the end of the discharge. The cell delivered 12.3 A.Hr to 2.0 volts. The behavior is quite expected and is shown in the thermogram (Fig. 14) of the cell against Al_2O_3. The differential temperature of the cell was measured at room temperature after turning on 0.25A through the previously discharged cell. The differential temperature showed a sharp exothermic rise corresponding to the sharp polarization of the cell voltage. On turning off the current, the differential temperature dropped back and a DTA run was started. The thermogram again showed the two typical exotherms at 101° and 110°. The beginning of the third one is barely noticeable at 168°C. Again, the repeat run (Fig. 15) showed only the beginning of an exotherm at 164°C.

All the discharged D cells were examined after the first DTA run and were found to have developed severe bulging of the cell top. The elapsed time between the discharge and the first DTA run was varied from 2 to 6 days and it did not seem to have any effect on the DTA thermogram. Similarly, the elapsed time between the first and the second DTA run was varied from 1 to 7 days and it did not affect the second thermogram.

C. Discussion

The relative stability of the undischarged $Li/SOCl_2$ cells is demonstrated by the lack of exothermic transistions in the DTA thermogram of undischarged D cells against Al_2O_3 reference. This corroborates the earlier DTA results (1) which showed the absence of any exothermic interactions between the materials present in a fresh cell in the temperature regime below the melting point of Li. The materials that are present in a fresh cell are Li,

glass, carbon, Teflon, Ni, $SOCl_2$, $LiAlCl_4$ and trace impurities.

The instability of the discharged $Li/SOCl_2$ cell is demonstrated by the presence of two strong exothermic reactions occurring in the temperature range of 80-100°C. The reactions are irreversible and may involve transient species since no exothermic transitions are observed during the repeat DTA runs. It is reasonable to conclude that some of the chemical species involved in these exothermic reactions are generated in the cell as a result of the discharge.
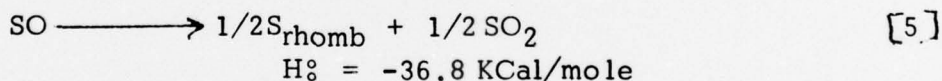
The primary cell reaction is thought to be:

$$2\ Li\ +\ SOCl_2\ \longrightarrow\ 2\ LiCl\ +\ SO \qquad [1]$$
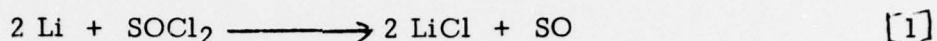
The bi-radical SO is thermodynamically unstable and may undergo further reactions as follows:

$$2\ SO\ \longrightarrow\ (SO)_2 \qquad [2]$$

$$(SO)_2\ +\ SO\ \longrightarrow\ S_2O\ +\ SO_2 \qquad [3]$$
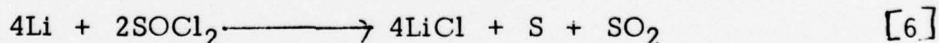$$\Delta H_o^o\ =\ -97.8\ K\,Cal/mole.$$
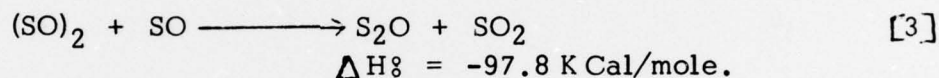
S_2O may polymerize to a yellow solid at low temperature. However, both the polymer and S_2O may undergo decomposition reaction on heating to 100°C or above in a quantitative manner.

$$2S_2O\ \longrightarrow\ 3S_{rhomb}\ +\ SO_2 \qquad [4]$$
$$\Delta H_o^o\ =\ -12.5\ KCal/mole\ of\ S_2O$$
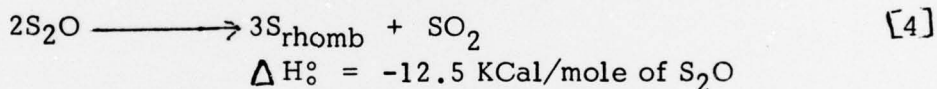
Thus, the overall decomposition reaction would be:

$$SO\ \longrightarrow\ 1/2\,S_{rhomb}\ +\ 1/2\ SO_2 \qquad [5]$$
$$H_o^o\ =\ -36.8\ KCal/mole$$

and the overall cell reaction:

$$4Li\ +\ 2SOCl_2\ \longrightarrow\ 4LiCl\ +\ S\ +\ SO_2 \qquad [6]$$

It is possible to calculate the thermodynamic EMF of the cell according to the reactions [1] and [6], using the $\Delta G°$ value of $SOCl_2$ in a gaseous state. The E_o calculated based on reaction [1] is 3.05 volt whereas the E_o calculated based on reaction [6] is 3.72 volt. The experimental value of 3.60 volt indicate further the instability of SO and that the cell voltage is probably a mixed potential corresponding to a mixture of reactions [1] through [5] depending upon the discharge temperature.

In view of the fact that the above E_o values were calculated using $\Delta G°$ of gaseous $SOCl_2$, the small difference between the experimental and the calculated value may indicate the reaction [6] to be the predominant overall cell reaction.

Based on this, the species that are thought to be formed as a result of discharge would be SO, $(SO)_2$, S_2O, $(S_mO)_x$ polymer, S, $LiCl$. Of these, all except $LiCl$ are reactive. The chemical reactions [3] through [5] are all exothermic and could cause the irreversible exothermic transitions observed in the DTA thermograms of the D cells. The reactions are also homogeneous (gas or liquid phase) and therefore they could occur at relatively high rates at room temperature.

In addition, the reactions of the above species with $SOCl_2$ and Li should also be considered. For example

$$2\ Li\ +\ S\ \longrightarrow\ Li_2S \qquad\qquad [7]$$
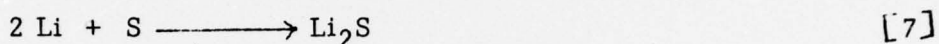
$$\Delta G° \ =\ -120\ KCal/mole\ of\ Li_2S$$

is an extremely exothermic reaction and is particularly prone to occur since S is in solution in $SOCl_2$. Furthermore, we showed (1) earlier that Li_2S undergoes spontaneous exothermic reactions with $SOCl_2$. We are in the process of determining the ΔH values for this reaction which is speculated to be

$$SOCl_2\ +\ Li_2S\ \longrightarrow\ S_2O\ +\ 2\ LiCl \qquad\qquad [8]$$
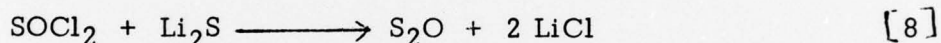
The nature of the "instability" generated in a thionyl cell by discharge is rather complex; although it manifests itself rather simply in the form of

       (a) Two exothermic peaks in the DTA of the discharged cell, and

       (b) Occasional spontaneous explosion of partially discharged cells on storage.

It is intriguing to speculate whether the two manifestations are related.

It is possible that the exothermic reactions, corresponding to those peaks in the thermogram, could occur at room temperature at a slower rate and build up heat locally inside the cell thereby accelerating the reactions even further thus providing a trigger for the remaining active materials such as Li, S, SO_2, $SOCl_2$ causing a thermal runaway. According to this model, the exothermic peaks and the occasional cell explosions are related. This suggests an interesting approach towards alleviating the spontaneous cell

explosion problem. Since, the second DTA runs do not show any exothermic peaks, it indicates that the chemicals responsible for the exothermic reactions are completely exhausted during the first run. Thus, a controlled thermal excursion may provide a means to deactivate the discharged cells.

III. Experimental Testing of "Hot Spot"
Theory of Cell Explosion

According to the "hot spot" theory, the spontaneous explosion of discharged Li/SOCl$_2$ cells is caused by a set of chemical reactions (discussed in the previous section) which creates a local "hot spot" in the cell by virtue of their exothermic nature and this "hot spot" then serves as a trigger for the other active cell components such as Li, S, SO$_2$, SOCl$_2$, Teflon and glass which fuel the thermal runaway. In order to test this theory we have attempted to create local "hot spots" inside the D cell by electrical means. The experimental details and the preliminary results are reported here.

A.   Experimental

Hermetic D cells were made with the electrode dimensions mentioned in the previous section of this report. The cell tops were fitted with G/M seals having sealed Kovar tube feedthroughs. The location of the three feedthroughs are shown in Fig. 16. The center feedthrough was used for electrolyte filling and as the anode terminal. The other two feedthroughs extended halfway down the cell and the tips were sealed by welding. The tips were fitted with heating wires as well as spark gaps. We carried out some experiments with automobile ignition coils and a power supply to generate spark between the tips of the two feedthroughs. Although, we were able to generate sparks in this manner, we were not successful in creating a thermal-runaway of a discharged cell by this means. We then continued our tests with heating wires connected between the tips of the insulated feedthroughs. We applied DC through the heating wire to generate local hot spots inside the cell. The cell voltage, the wall temperature and the temperature at the tip of the feedthroughs where the heating wire was connected were monitored during these experiments.

B.   Results and Discussion

We tested six cells having heating wires located near the cathode side within the electrode coil. The Li anode was electrically insulated from the heating wire by the separator.

The first cell had been completely discharged at 0.25A yielding a capacity of 12 A.Hr. The local hot spot was created by passing 3A through the heating wire for 0.6 minute. During that time the cell wall temperature rose to 26° and the tip temperature rose to 53°, at which point an electrical discontinuity developed in the heating wire. There was no cell explosion.

The second cell was completely discharged at 0.1A yielding a capacity of approximately 15 A.Hr. The local hot spot was created by passing 3A for 1 minute, in which time the tip temperature rose to 55°C. The current was then increased to 4A; the tip temperature rose to 75°, the wall temperature to 28° in 0.3 minute and the heating wire fused and disconnected at that point.

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The cell voltage of 3.68 volt indicated that there was no cell shorting. There was no explosion.

The third cell was discharged completely at 0.25A to a capacity of 13.4 A.Hr. The cell was internally heated using a 3A current through the heating wire for 95 minutes. During that time, the cell wall temperature rose to 63° and the tip temperature rose to 107°. Nothing happened. Next day, the cell was subjected to internal heating starting at 3A and then increasing to 7A in increments of 1A at 1 minute intervals. At 7.0A, the heating wire fused in 0.3 minute, causing the cell to develop internal short and thereafter both the cell voltage and the cell temperature gradually declined with time without any explosion.

The fourth cell was partially discharged at 0.5A to a capacity of 8 A.Hr and then subjected to internal local heating at 3A for 1 minute followed by 4A for 1 minute, then 5A for 2 minutes and 6A for 3 minutes. During the 5A heating, the heating wire failed and caused an internal short. The OCV of the cell dropped to 3.50 volt indicating a high resistance short. The wall temperature rose to 40°. The current was shut off for a few minutes during which the wall temperature kept on rising slowly. After this we heated the cell again starting at 3A and increasing to 8A in 1A increments in 1 minute stages. The cell wall temperature rose to 52° and the tip temperature was 72°C. The cell was then kept at room temperature for 22 hours during which time the cell voltage gradually declined from 3.60 volt to 2.2 volt due to the discharge through the internal short near the heating wires. The wall temperature dropped to 31°C and the tip temperature dropped to 33°C. At that point we turned on the internal heating using 4A and the cell exploded in less than 2 seconds.

The above exploratory experiment provides some support for the "hot spot" theory. The discharge of the cell through the internal short near the heating wire may have caused the accumulation of the active discharge products such as S, S_2O, $(SmO)_x$, etc. near the heating wire. The subsequent heating with 4A caused these products to ignite very quickly thus resulting in an explosion. The failure of the other three cells to explode was probably due to the fact that the discharge products were distributed uniformly throughout the cathode and were not concentrated enough near the heating wire to explode. Also, in those experiments, the cells were discharged 3 to 8 days prior to the heating experiment and the active discharge products may have been distributed evenly by diffusion and were not in sufficient concentration near the heating wire to ignite.

In the case of the fifth cell which was discharged at 0.1A yielding a capacity of approximately 15 A.Hr, the heating wire broke off on 3A heating without shorting the cell. No explosion occurred.

The sixth cell was internally heated without discharging it previously. The heating started at 3A and increased to 5A in 1A increments with 1 minute stages. The heating wire broke off at 5A within 0.2 minute. At that point the wall temperature was 30° and the tip temperature was 77°C.

We plan to continue these experiments in order to develop electrical heating conditions which will simulate the chemical ignition of the discharged cell that undergo thermal runaway. Once we know how to cause the thermal runaway of a discharged cell in a reproducible manner, we then will be able to test various concepts of alleviating the explosion problem in D cells.

IV. Conclusions and Future Work

The instability of the discharged Li/SOCl$_2$ D cells was characterized using the DTA technique. The DTA thermogram of a discharged D cell showed two sharp exothermic transitions in the 80-100°C temperature range corresponding to exothermic reaction of the discharged products. The absence of these peaks in repeat runs indicates the possible exhaustion of the reactive species during the first run. This suggests a possible approach of deactivating the discharged cells by subjecting them to a controlled thermal defusing.

Experimental evidence has been obtained to provide aleatory support for the "hot spot" theory of cell explosion.

We plan to refine the experimental techniques to create local hot spots inside the D cells. We plan to study the effect of location, the duration and the intensity of the hot spots on the explosion of D cells. Once we know how to initiate cell explosion by artificially created local hot spots in a controlled manner, we will then be able to evaluate various concepts for preventing the spontaneous explosion of discharged Li/SOCl$_2$ cells.

V. References

1. A. N. Dey, "Sealed Primary Lithium Inorganic Electrolyte Cell", Interim Report, ECOM-74-0109-13, November 1977.
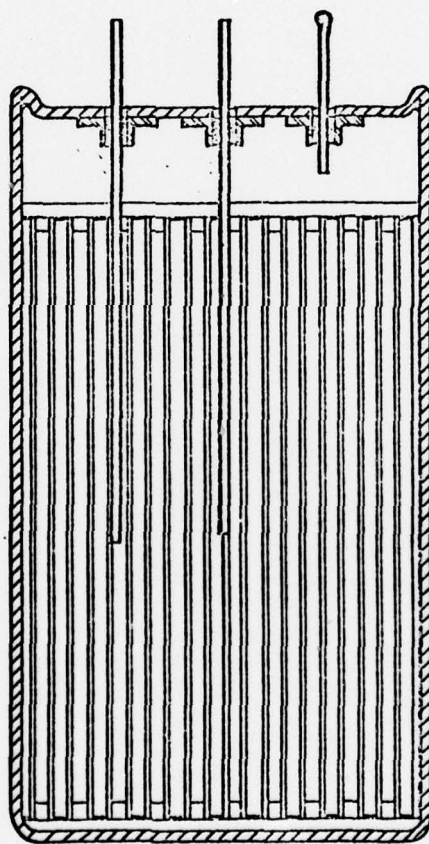
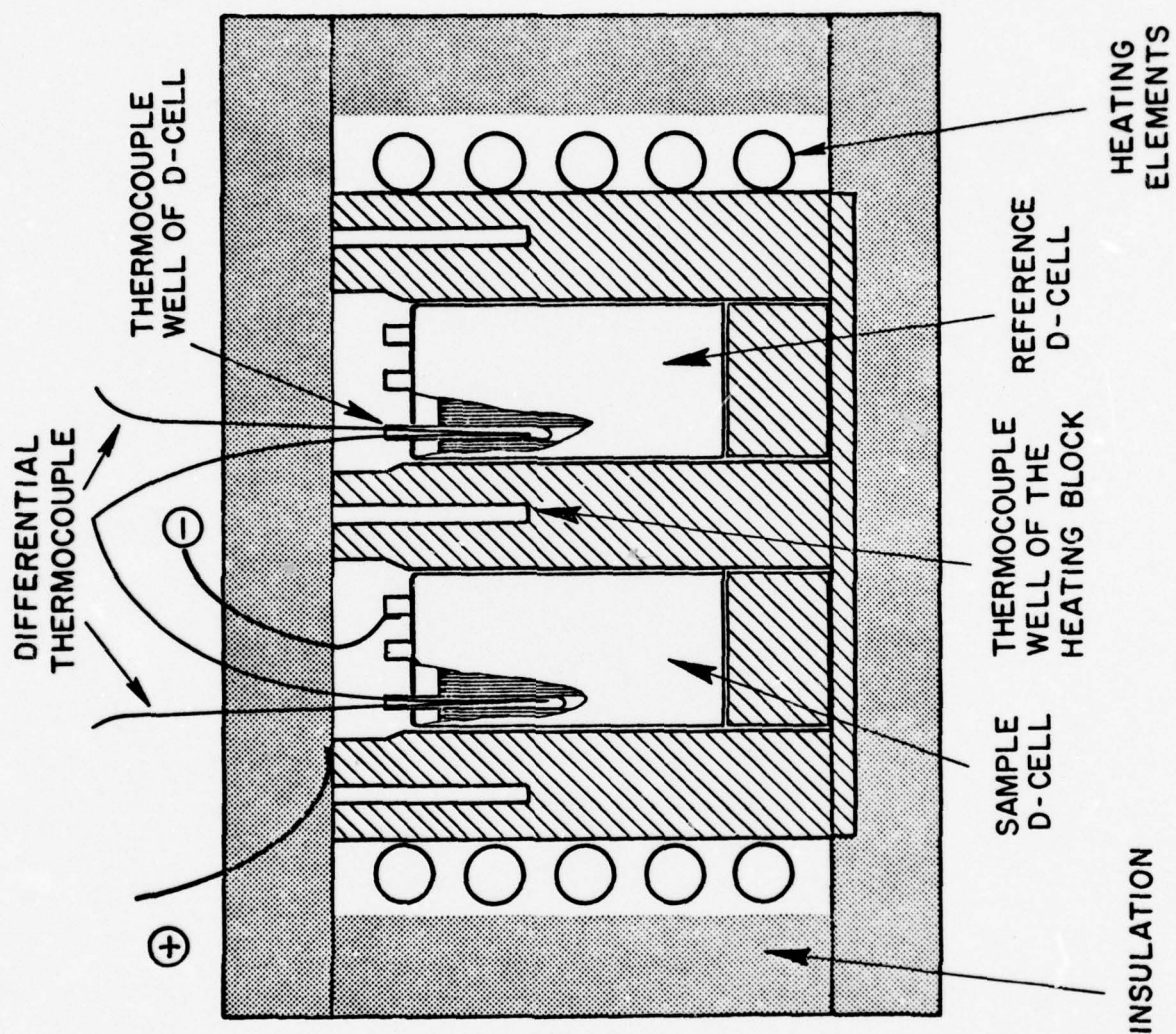Fig. 1   Cross sectional view of the $Li/SOCl_2$ D cell with thermocouple
wells

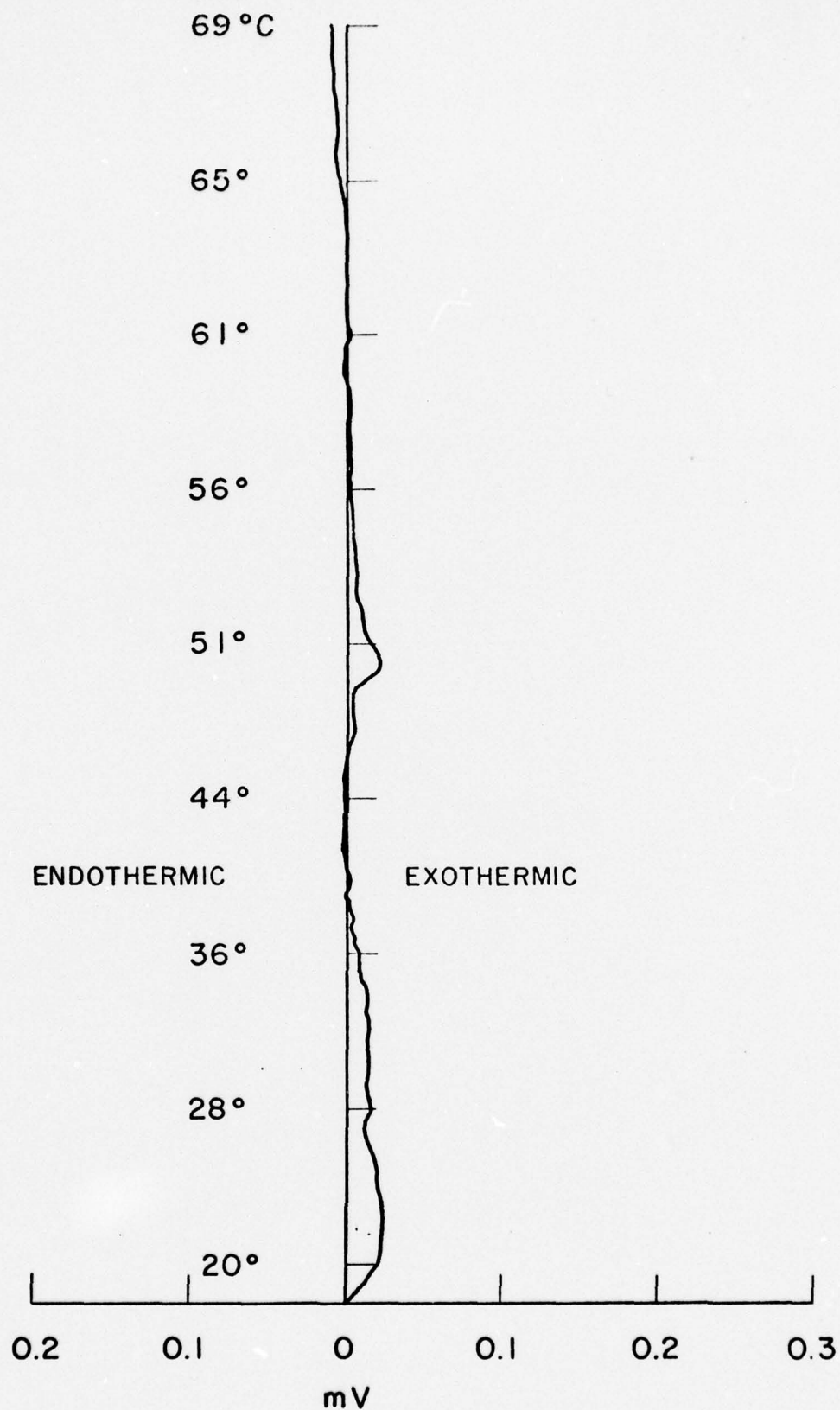Fig. 2   Fixture for DTA of Li/SOCl$_2$ D cells
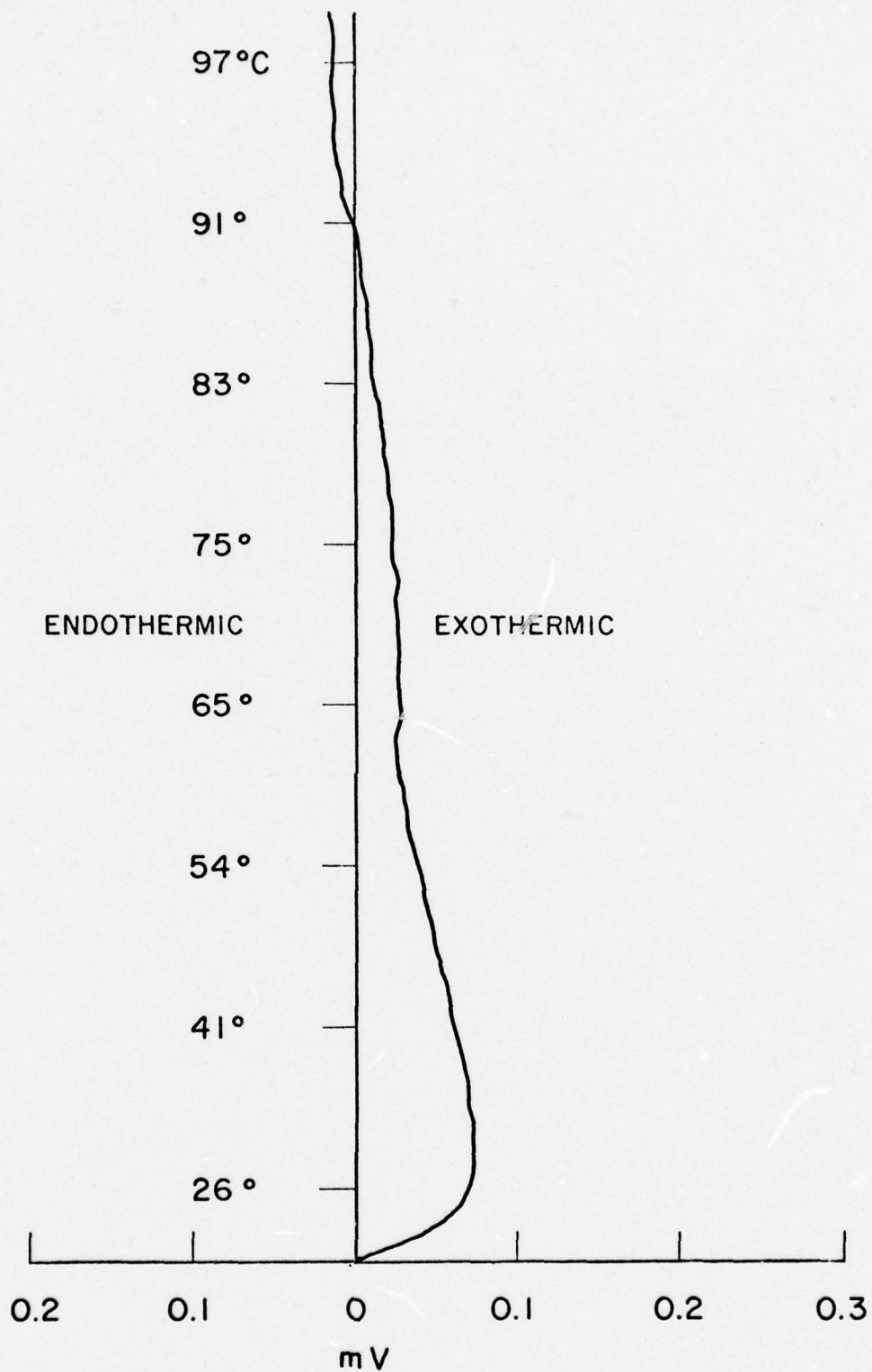
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Fig. 3   Thermogram of two fresh Li/SOCl$_2$ D cells

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Fig. 4   Thermogram of a fresh $Li/SOCl_2$ D cell against a D size can
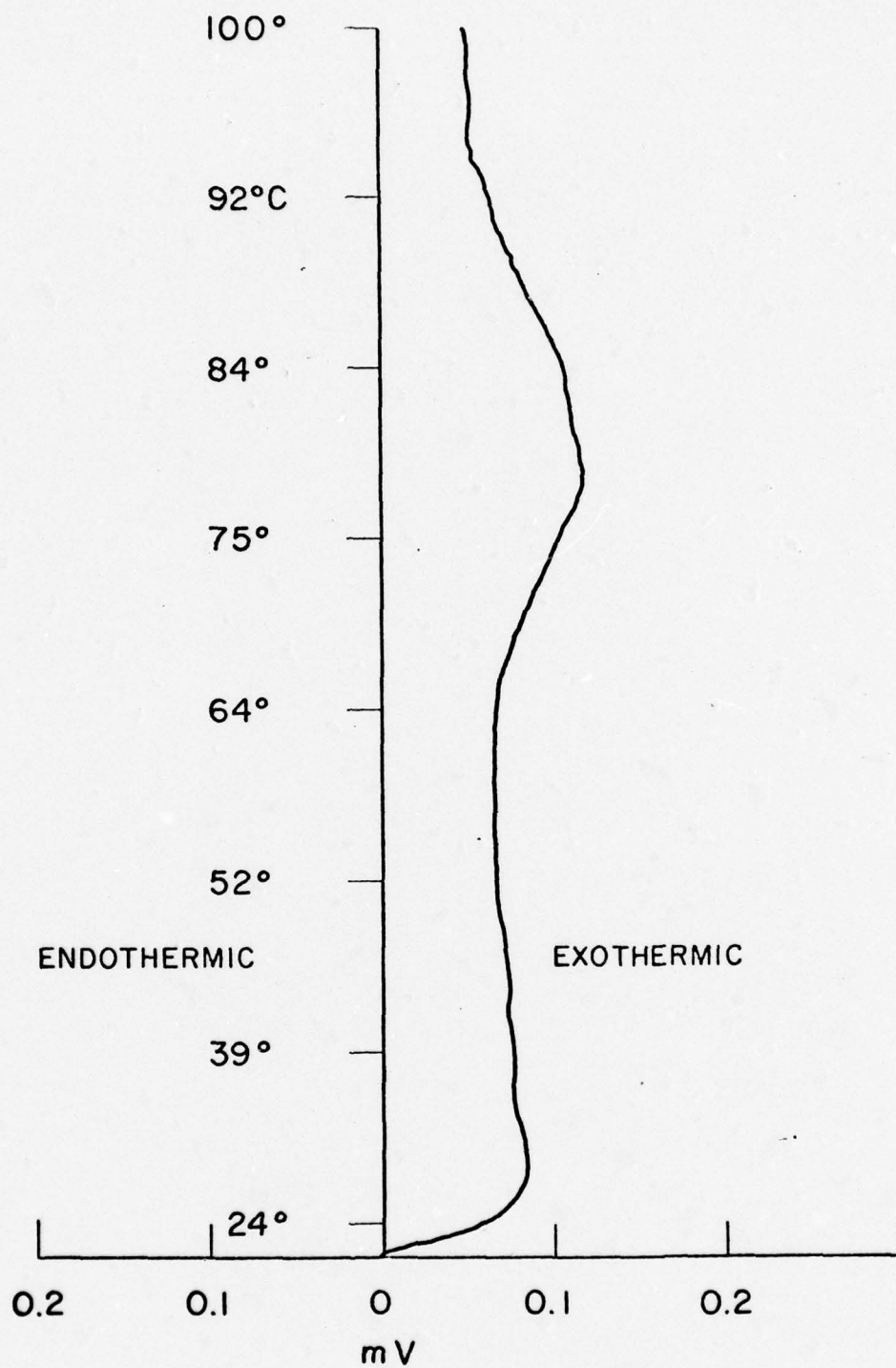filled with Al_2O_3

17

Fig. 5 Thermogram of a partially discharged (6 A.Hr) Li/SOCl$_2$ D cell against Al$_2$O$_3$

18
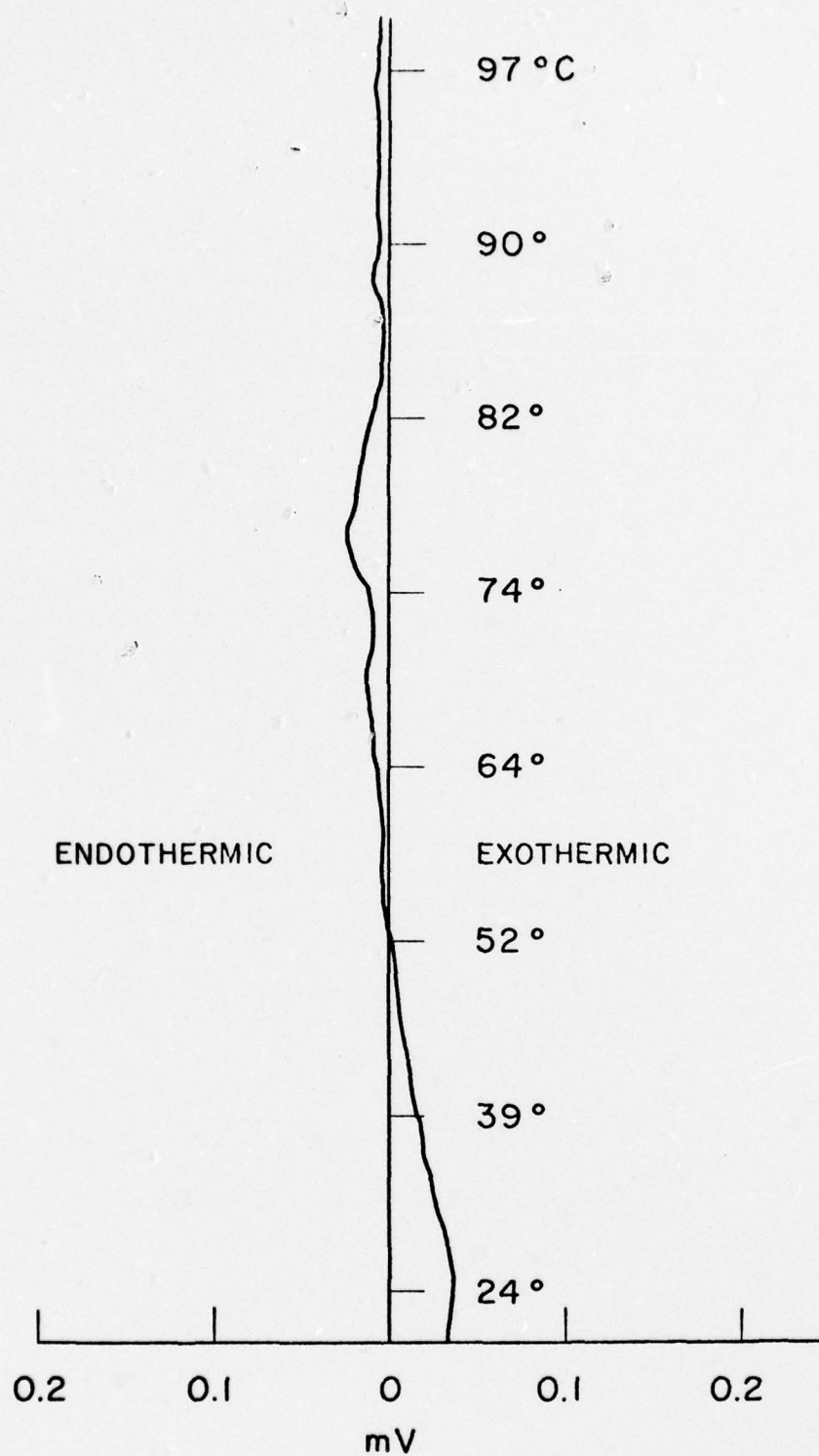
Fig. 6   Thermogram of the partially discharged (6 A.Hr) D cells (second run) against a fresh D cell
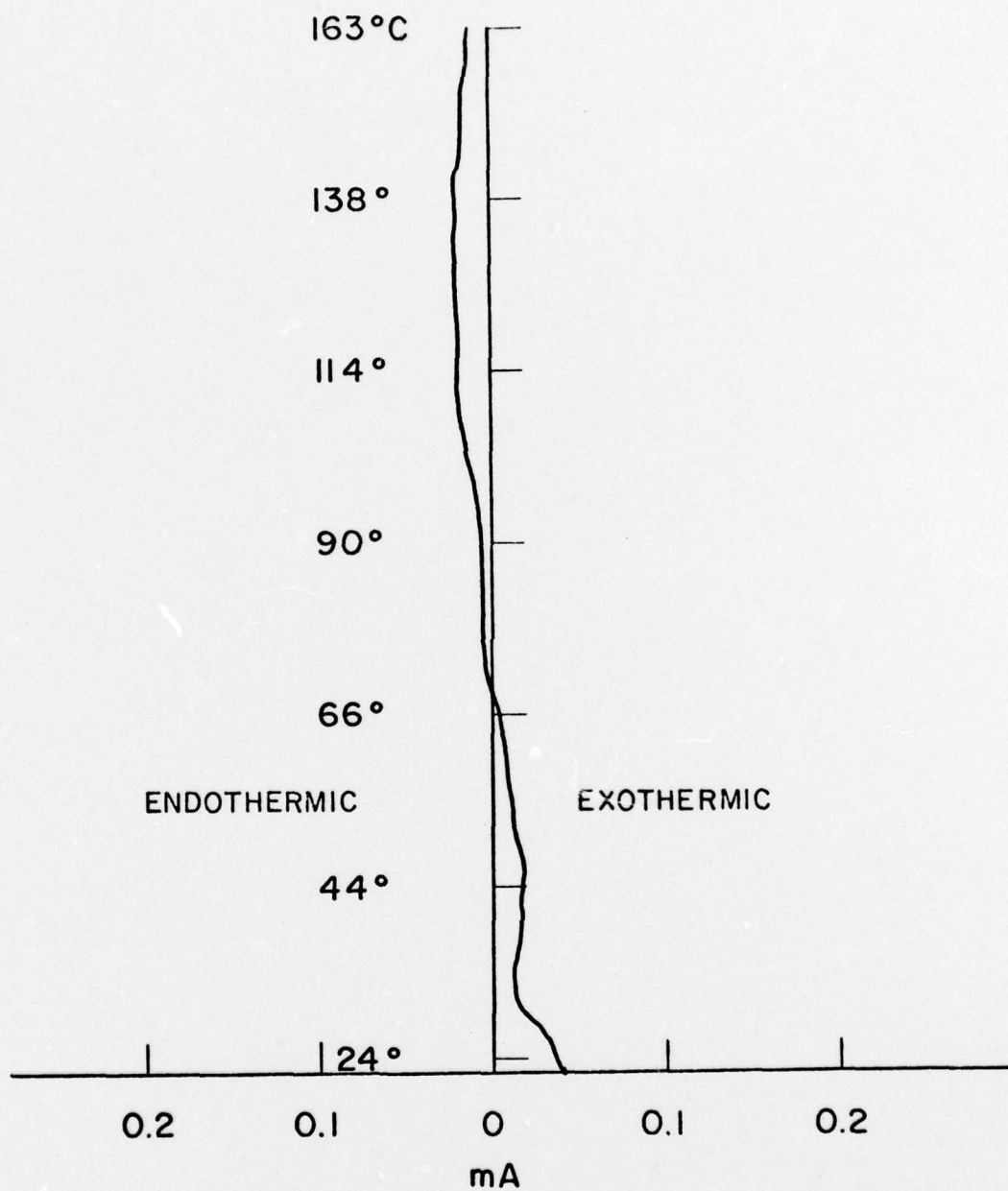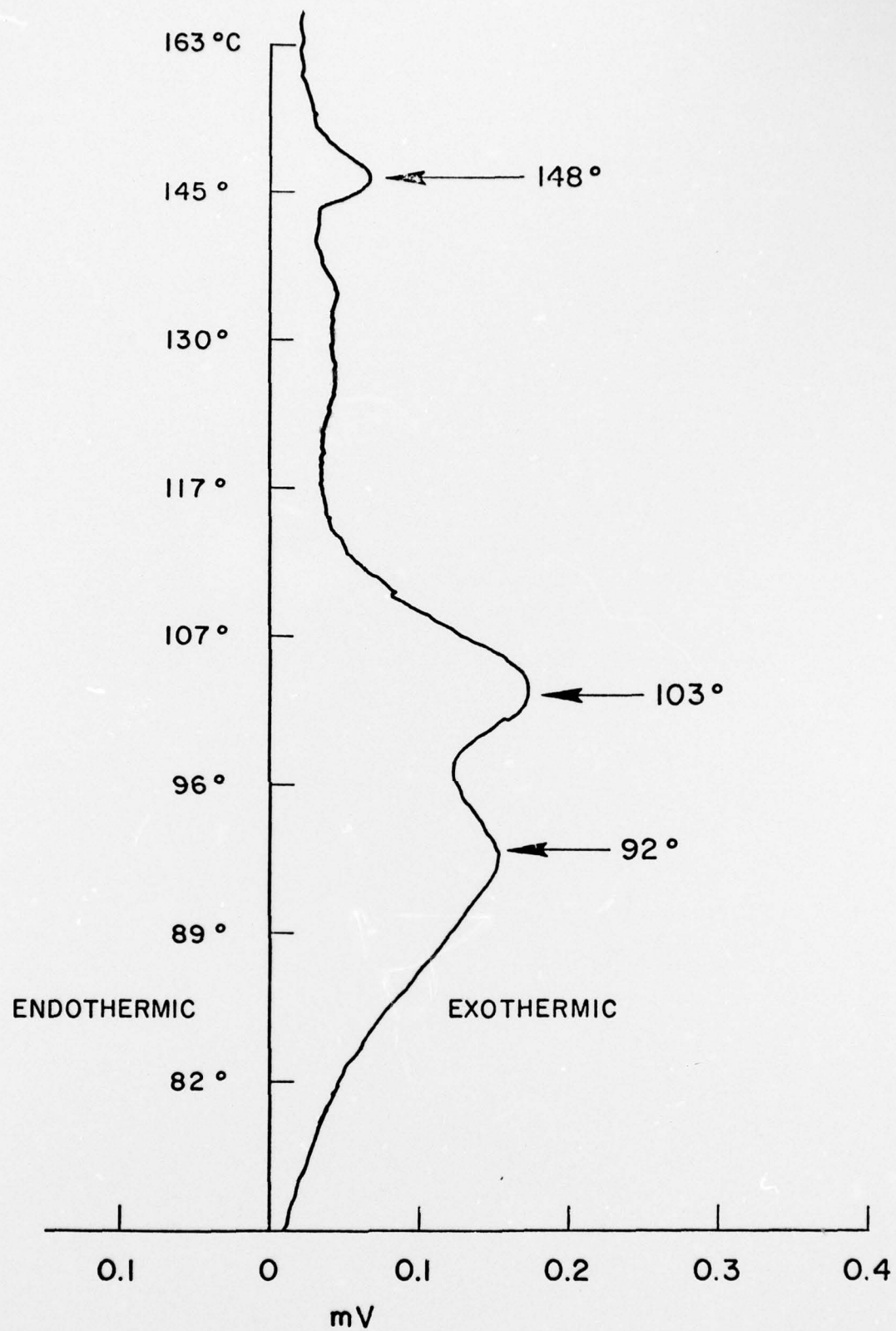
Fig. 7   Thermogram of two fresh Li/SOCl$_2$ D cells

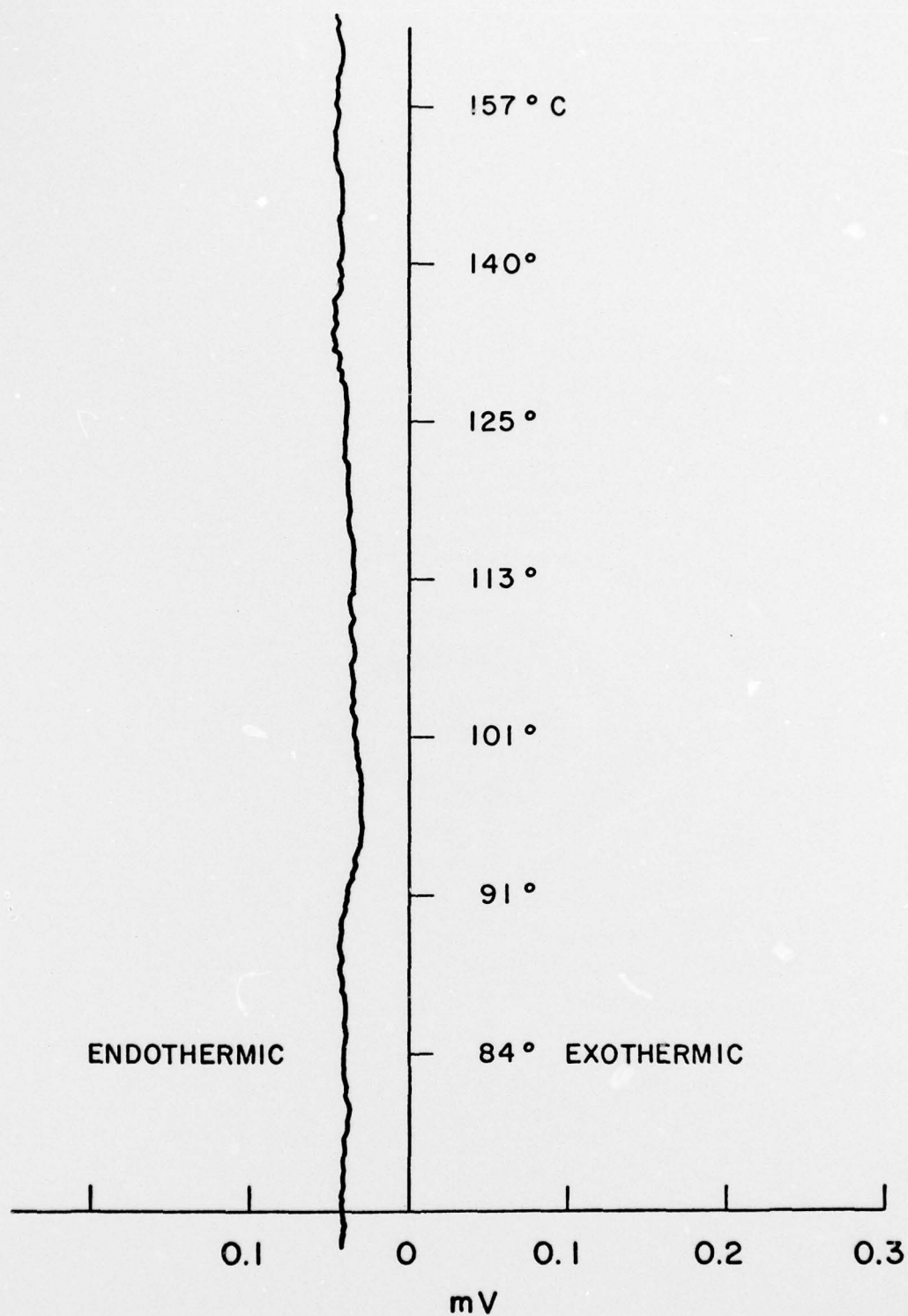Fig. 8 Thermogram of a completely discharged (13.1 A.Hr) D cell against a fresh cell

21

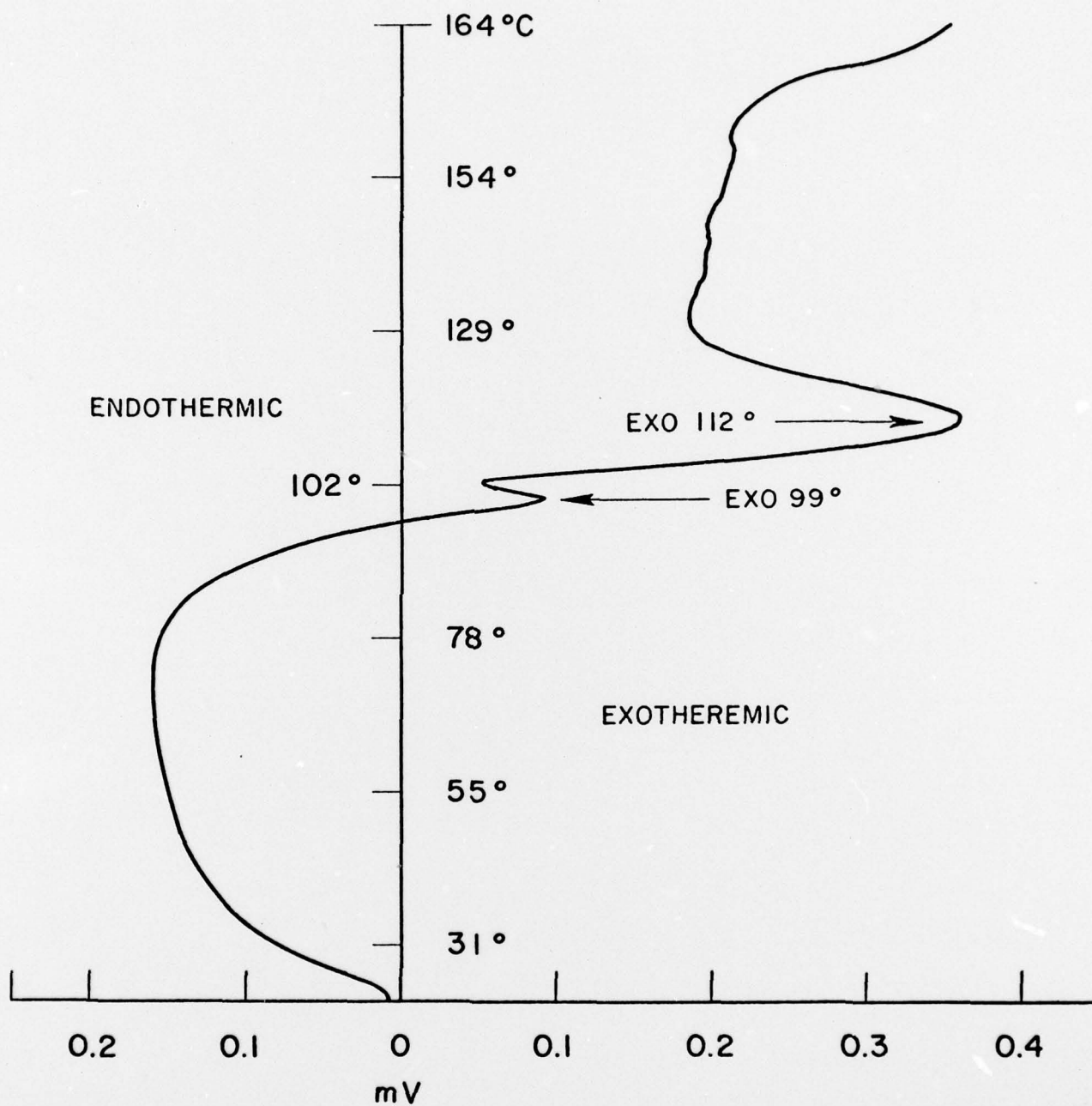Fig. 9   The repeat run of the cells shown in Fig. 8

22

Fig. 10   Thermogram of a completely discharged (12.7 A.Hr) D cell
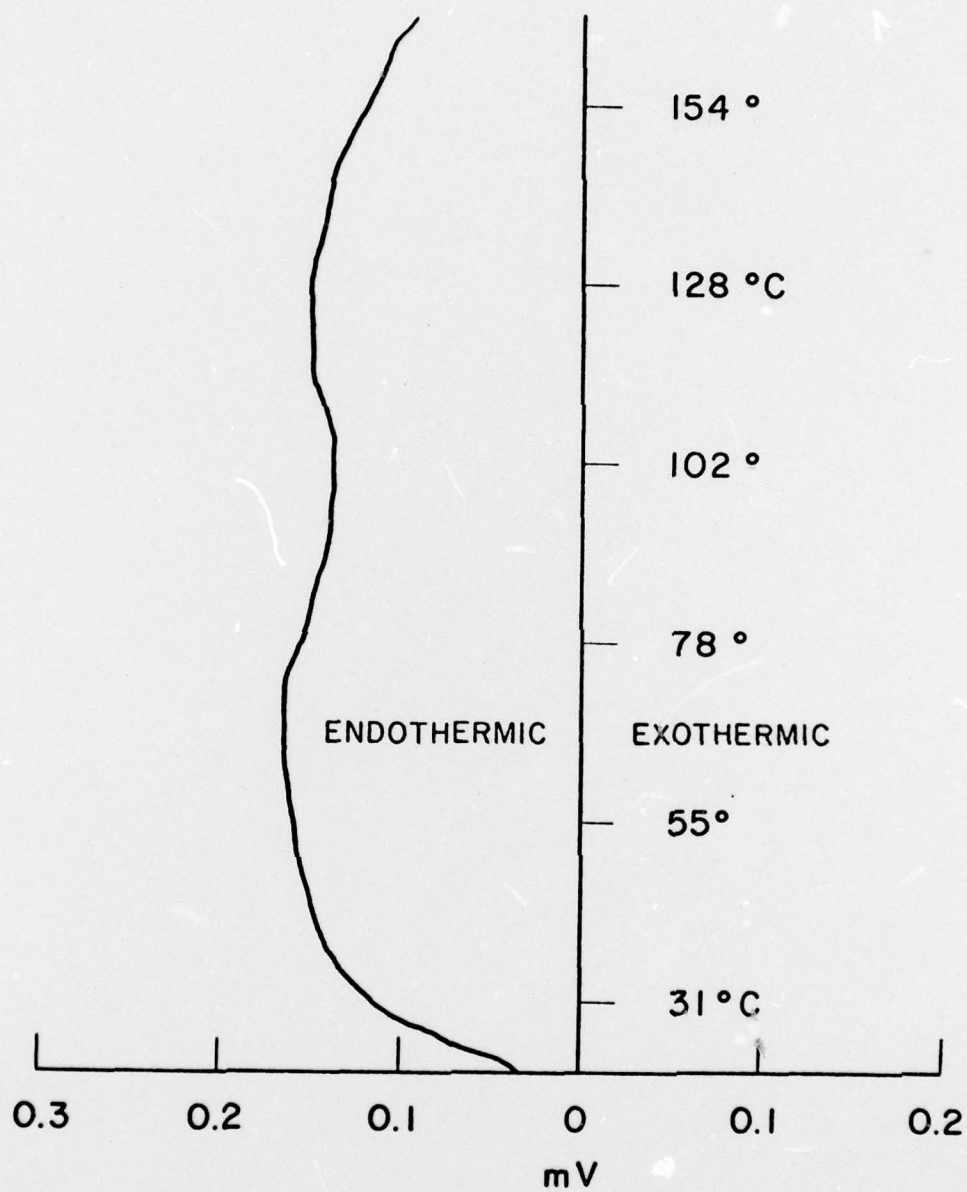against a fresh cell

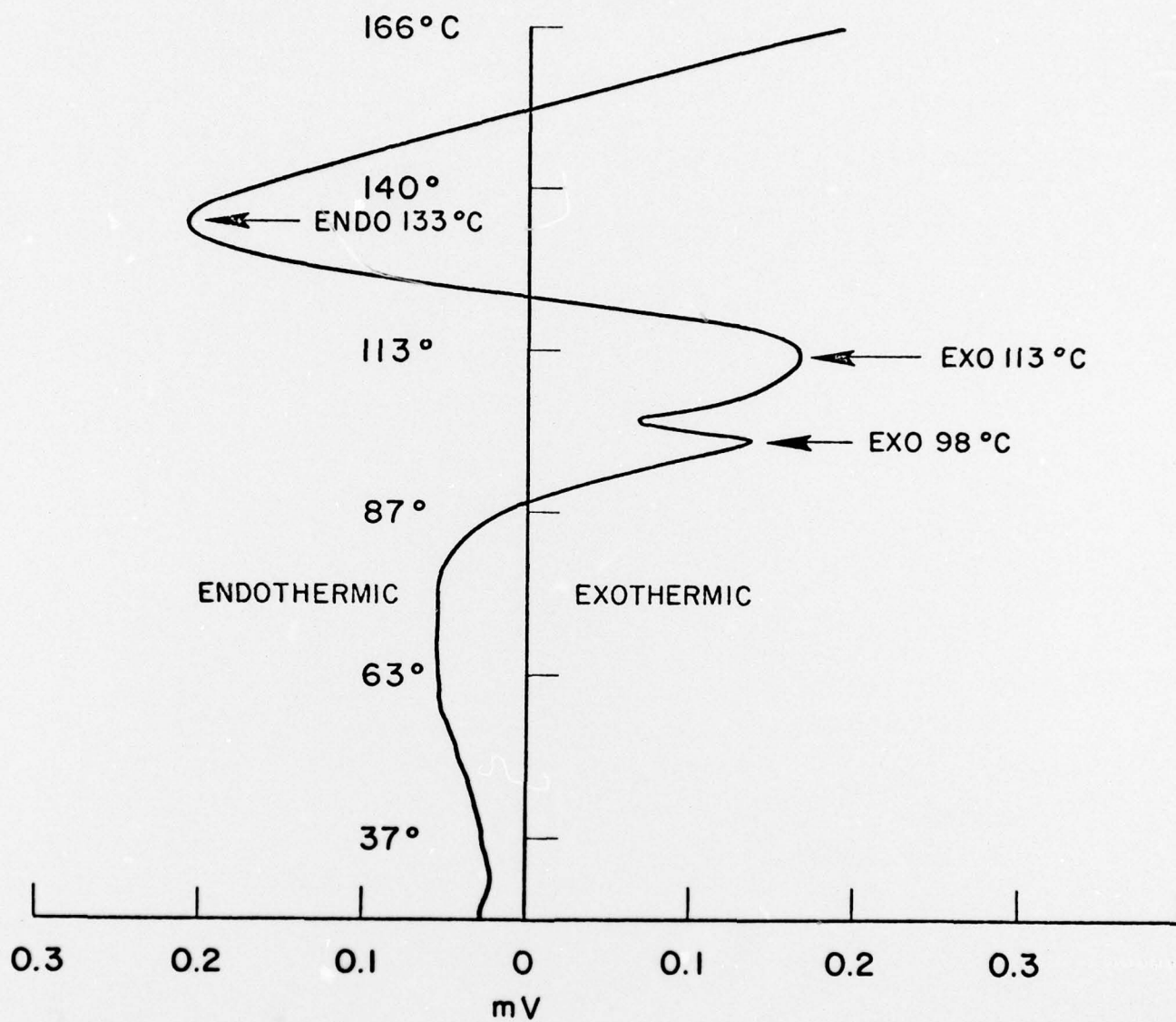Fig. 11 The repeat run of the cells shown in Fig. 10

Fig. 12 Thermogram of a completely discharged (12 A.Hr) D cell against Al_2O_3
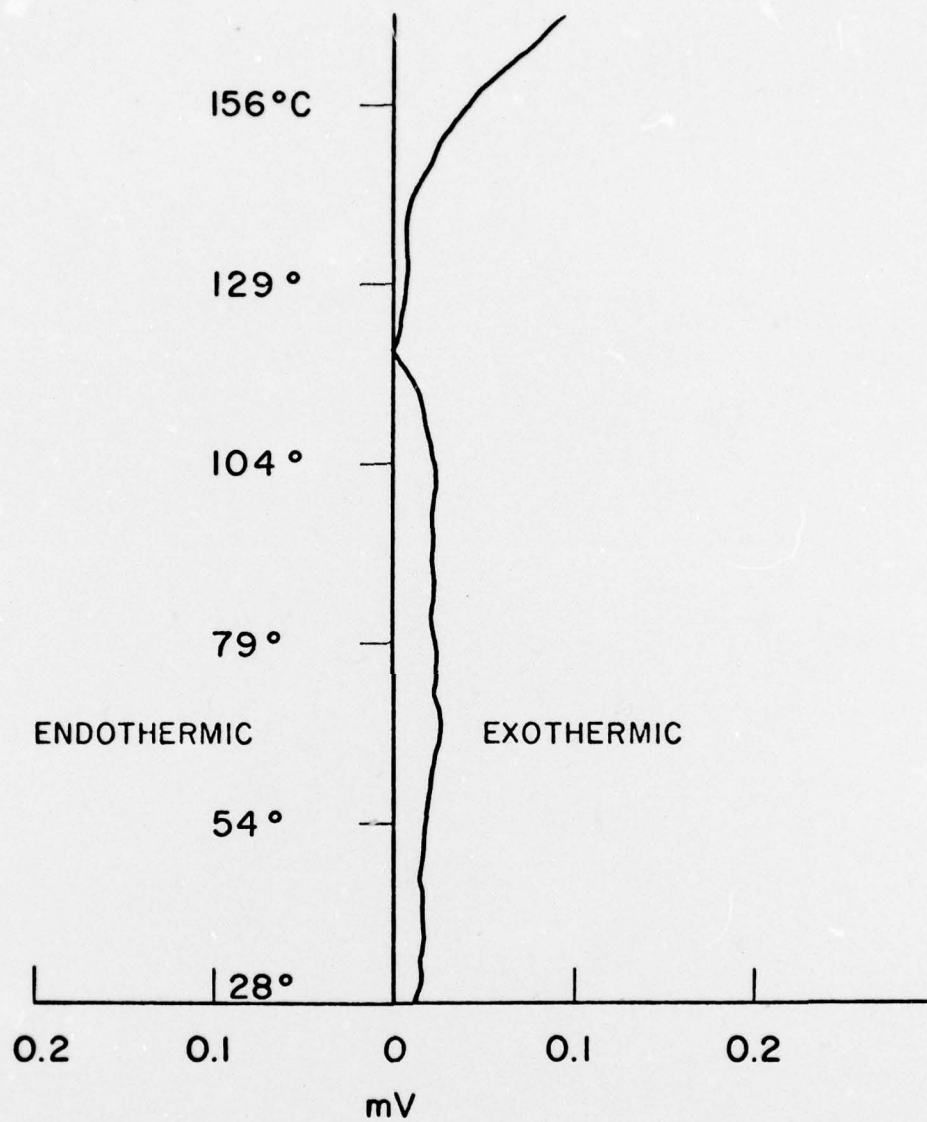
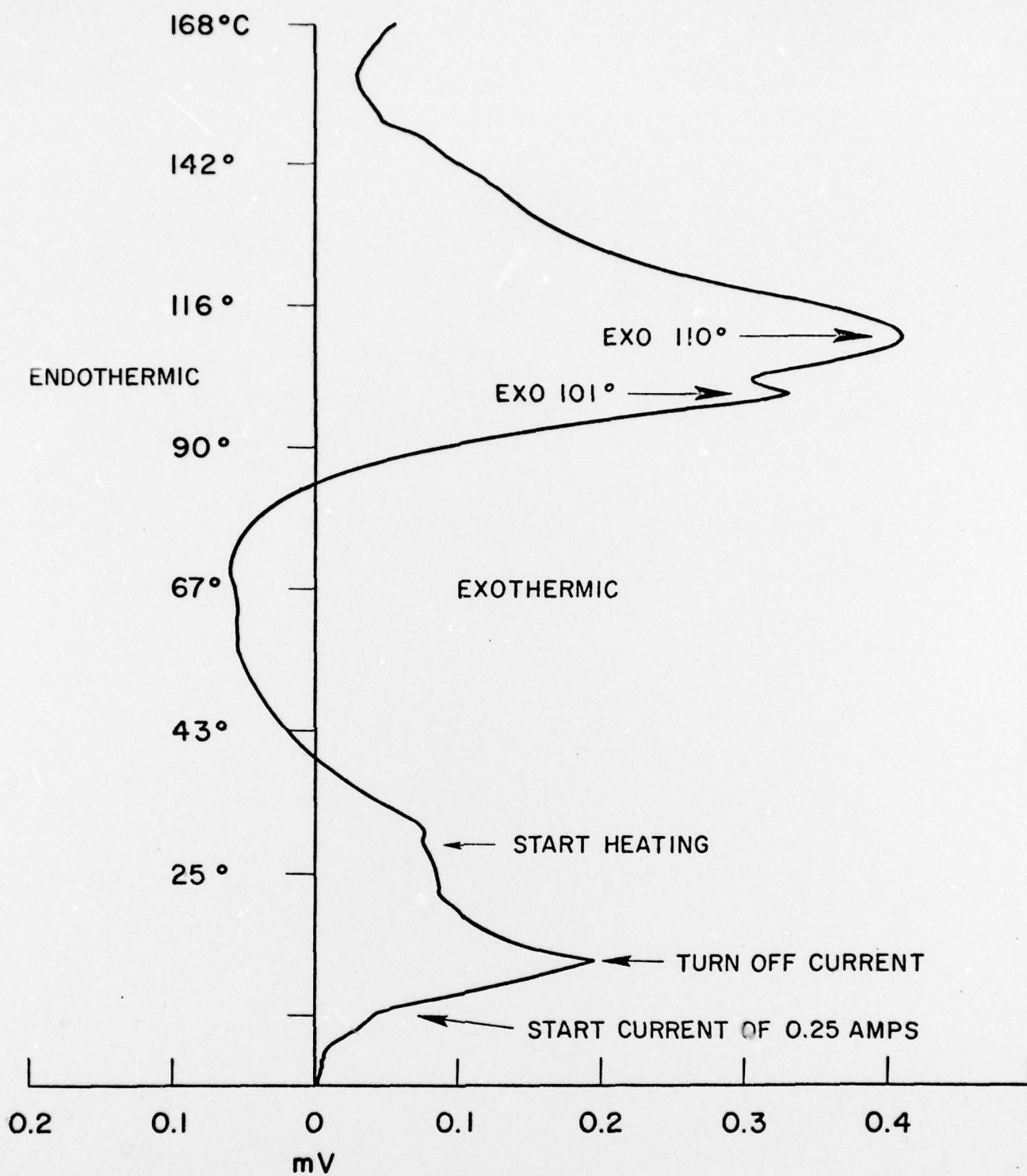Fig. 13   The repeat run of the cell shown in Fig. 12

Figure 14 The thermogram of a completely discharged (12.3 A.Hr) D cell against Al_2O_3, showing the effect of overdischarge on the differential temperature
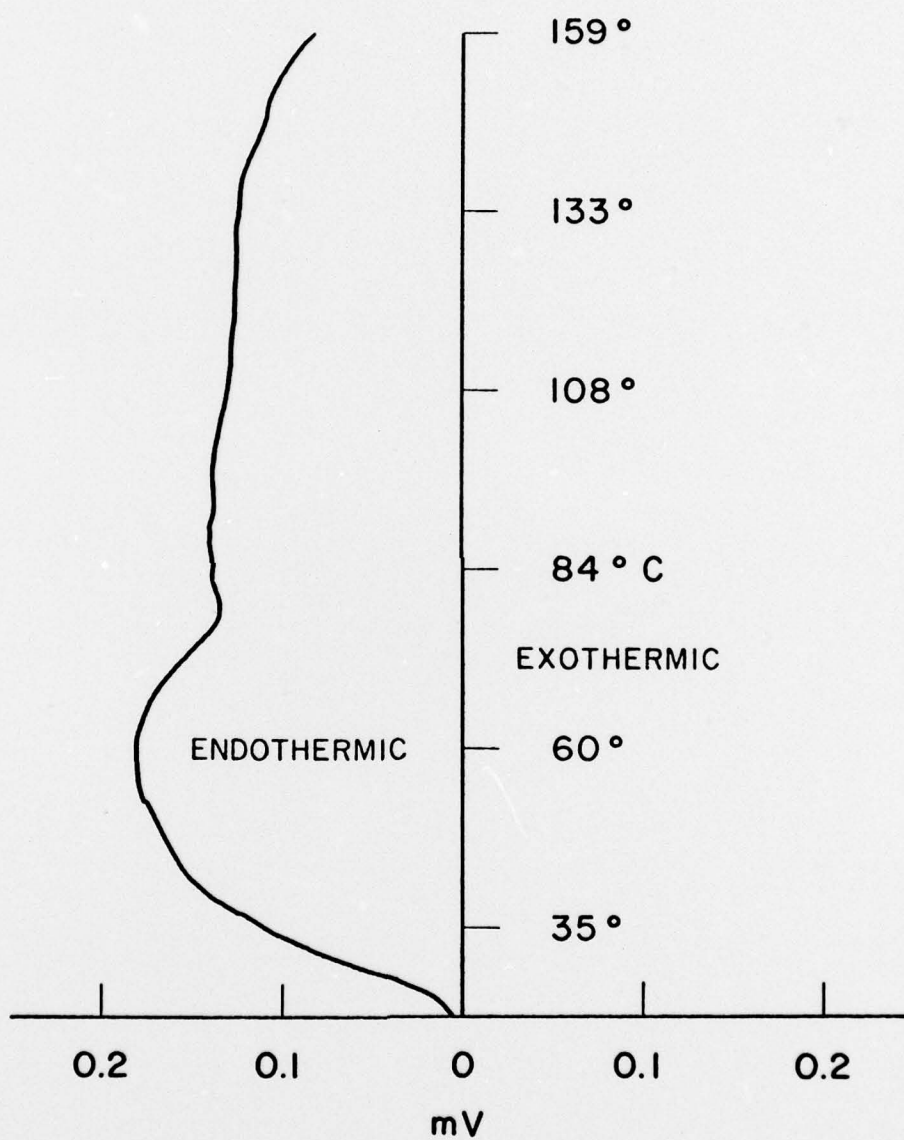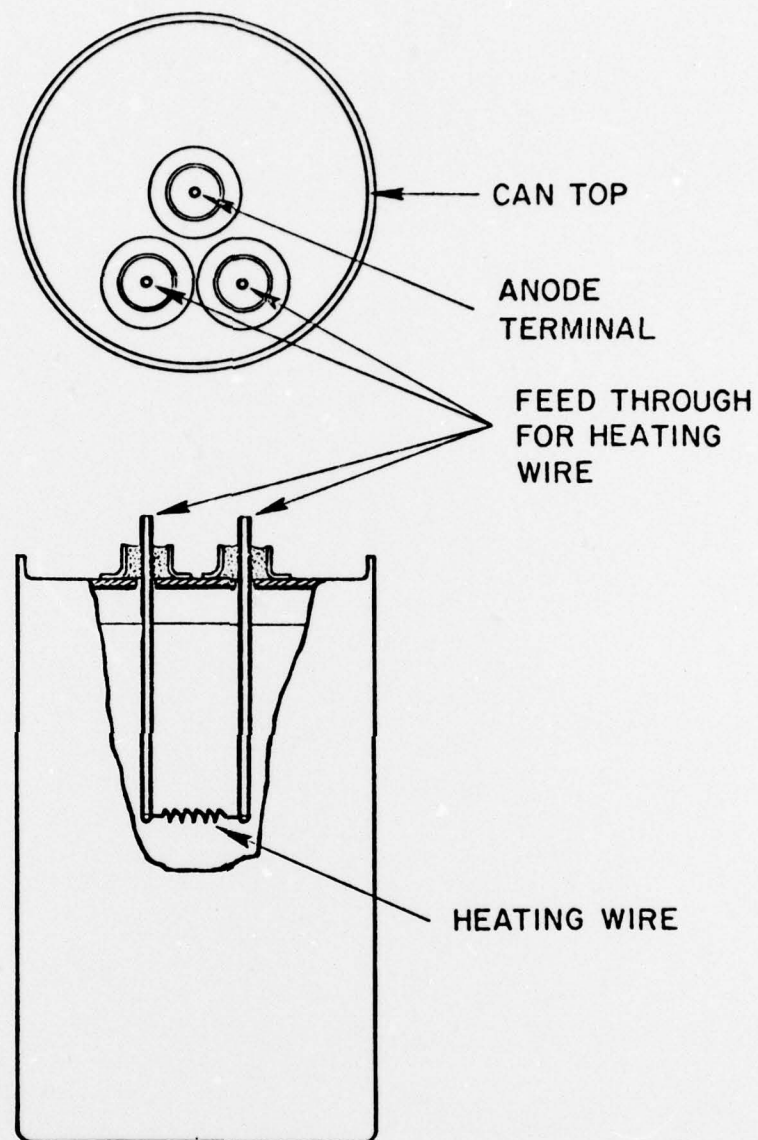
Fig. 15   The repeat run of the cell shown in Fig. 14

Fig. 16   The schematic representation of the D cell showing the feedthroughs for internal heating

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